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31 Quality of Frozen Fish

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Abstract Freezing is the most widely used preservation method for fish. The quality of seafood depends on the freezing rate. Different factors affect the quality of frozen fish. These parameters are biological or depend on the conditions of catching and processing fish.

The freeze or cold chain must be kept unbroken during storage and transport. Attention must be paid to retail display equipment and temperature monitoring.

The frozen state of fish has an impact on microorganisms. Freezing also influences biochemical attributes: fat and fat decomposition, oxidative rancidity, and protein changes. Sensory attributes are altered by freezing. How can these sensory changes be monitored? Fish populations belonging to the same fish species may have differences in freezing quality. Finally, freezing also has an impact on physical attributes.

Prefreezing factors and postfreezing treatments influence or protect the storage of frozen fish.

Keywords: Frozen fish quality, practical storage life (PSL), high-quality life (HQL), freeze chain, QIM, freezing process, fish rigor mortis, fat decomposition, oxidative rancidity, fish glazing

31.1 INTRODUCTION

Seafood quality, including safety, is a major concern facing the seafood industry today and is also one of the most abused words in food science, especially in fisheries and aquaculture research. A number of surveys have shown that consumer awareness about the quality of food is increasing. Fish and fish products are in the forefront of food safety and quality improvement because they are among the most internationally traded food commodities (Gonçalves & Blaha 2010).

Freezing is the most widely used preservation method for fish and it accounted for a 49.8% share of total processed fish for human consumption and 20.5% of total fish production in 2008 (FAO 2010). Nevertheless, the eating quality of fresh fish (not frozen before being sold on the market) is considered superior to that of frozen fish. It is, however, possible to produce frozen fish of high eating quality by quickly freezing the fish and subsequently storing it at low and stable temperatures. In this way, the physical and chemical processes causing the quality of the fish to deteriorate may be reduced. Quality deterioration is seen, for example, in the development of ice crystals, oxidation of fat, and degradation of muscle protein. The effect of freezing and frozen storage has also been studied for a few years and is described in a number of reviews (Sikorsky *et al.* 1976; Shenouda 1980; Haard 1992; Love 1992; Mackie 1993;

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Table 31.1 Storage time for PSL and storage time for HQL stated in months for lean fish (cod), big fatty fish (salmon), and small fatty fish (herring).

	Shelf life in months			
	−18°C		−30°C	
Fish species	PSL	HQL	PSL	HQL
Lean fish (e.g., cod)	7	3	12	6
Big fatty fish (e.g., salmon)	7	3	18	6
Small fatty fish (e.g., herring)	5	2	10	5

Sikorsky & Kolakowska 1994). Part of this chapter has also been published in Danish by Jessen and Nielsen (2002).

Frozen fish is easily stored and distributed. Under ideal circumstances (low and stable storage temperatures), some fish species may retain a fair eating quality for over a year. Shelf life can be assessed either in terms of practical storage life (PSL) or high-quality life (HQL). PSL is defined as the time the product can be in cold storage before it loses its characteristic properties or becomes unsuitable for consumption. PSL is often determined between trade partners, and no legislative rules apply to this area. HQL is a target for how long the product can be in cold storage before taste panels are able to discern a clear difference from the original quality of the fish. HQL is normally two to three times shorter than PSL. PSL, moreover, is what is eventually declared on the product. The shelf life of fish in cold storage depends on time, temperature, and the species of fish (Table 31.1).

Frozen fish can be marketed as super chilled, frozen thawed, freeze chilled, or refreshed with and without modified atmosphere packaging (Bøknæs *et al.* 2000; Olafsdottir *et al.* 2006).

Super chilling (partial freezing) extends shelf life by cooling the fish down to 1–2°C below the freezing point (Magnussen *et al.* 2008). The surface is thereby frozen and protects the fish by inhibition of microbial activity. Super chilling has been described as early as 1920 but has mostly been used to ease the slicing process of, for example, smoked salmon. Super chilling can be used to protect against temperature rises in poor cold chains for a short period. If the cold chain is out of control for a longer time, microstructural changes of the tissue are caused by ice crystallization and recrystallization causing extended drip loss resulting in a dry and tough product.

A frozen thawed, refreshed, and freeze chilled fish is a fish that has previously been frozen and thawed either before packaging and distribution or thawed during distribution. The quality of freeze chilled fish is dependent on the quality of the frozen fish and the thawing process. The process enables the manufacturing of bulk products to be released into the chill chain on demand (Fagan *et al.* 2003; Jensen *et al.* 2010).

31.2 THE FREEZING PROCESS—FROM WATER TO ICE

31.2.1 Seafood quality and freezing rate

Fish muscle contains a large amount of water, often about 80%, and on cooling below the freezing point of the tissue fluids (*c.* −1.5°C), water in the fluid is converted into ice (Fig. 31.1). As ice forms, proteins and solutes become concentrated in the nonfrozen fraction. The freezing point of the nonfrozen fraction is depressed as the solute concentration increases. Ultimately,

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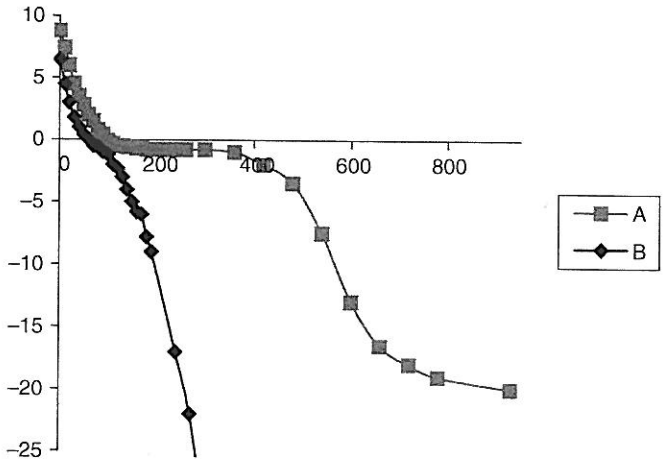

Fig. 31.1 Temperature profiles during freezing of whole cod. (A) Freezing at −20°C in still air (home freezer). (B) Freezing at −45°C in air blast freezer (industrial freezer). The temperature was measured in the center of the fish (core temperature). It is apparent from the figure that the fish can be brought through the critical temperature interval, from 0°C to 5°C, when quick freezing takes place at a low temperature and when a fan at the same time makes sure that the heat from the fish is removed quickly from the surface.

Table 31.2 Variation of percentage of water that remains unfrozen for cod fillet.

Temperature (°C)	% Unfrozen water
−1	92
−2	48
−3	33
−4	27
−5	21
−10	16
−20	11

Source: From Hedges and Nielsen (2000).

the freezing point of the nonfrozen fraction equals that of the freezing temperature. Once this point is reached, equilibrium is established between the ice phase and the nonfrozen fraction. The amount of nonfrozen fraction depends upon the composition of the fish product, and on the temperature at which the product is frozen or stored. When about 75% of the water is frozen, the temperature once more starts to drop rapidly. The lower the temperature (at −30°C), the more ice is formed (about 90% of water turns into ice) and the more concentrated the solutes become. Conversely, on increasing the temperature the amount of nonfrozen water increases (Gonçalves & Blaha 2010).

Table 31.2 shows the amount of unfrozen water in cod fillet as a function of temperature. As a consequence of forming a highly concentrated nonfrozen phase, potential reactants (e.g., enzymes and substrates) become far more concentrated than in the living tissue. Reactions are, potentially, accelerated. However, lowering the temperature decreases the rates of these reactions. Therefore, two antagonistic effects occur on cooling: an increase in reaction rate due to freeze concentration and a decrease in reaction rate due to a lowering of the temperature. In addition, in some foods, reaction rates may become diffusion controlled (Hedges & Nielsen 2000).

The actual freezer design and operation must compromise between quality and cost criteria. Unfortunately, the value of quality is difficult to quantify. Quality is usually considered to be related to freezing rate due to the latter's effect on ice crystal location and size and weight loss, but the relationship is ill-defined and very product specific. For most foods, as long as the freezing rate is "reasonably" fast, quality requirements become secondary to cost issues. Exceptions are usually frost-sensitive or valuable foods. Given that many of the advantages of fast freezing can be lost during subsequent storage, often too much emphasis is given to achieving the highest freezing rate in the process freezer. It is probably more critical that complete product freezing is achieved in the process freezer because rates of temperature reduction in frozen storage are much lower and can lead to both significant loss of product quality and increased storage freezer refrigeration costs (Cleland & Valentas 1997).

It is now well known that rapid freezing is essential for good quality. This is defined as taking no more than 2 h to pass from 0°C to −5°C (from 32°F to 23°F) in the thickest part of the fish, and freezing at this rate or faster is now normal good commercial practice. Most fish begin to freeze at about −1°C (30°F), but the multiplication of the putrefactive bacteria is only completely arrested at about −9°C (15°F). Although bacterial spoilage is then suspended and there is some reduction in bacterial numbers, not all the bacteria are destroyed by freezing (Ranken *et al.* 1997).

Freezing rate affects the rate of tenderizing after thawing but not the ultimate tenderness. Freezing at −10°C more than doubles the rate; freezing in liquid nitrogen almost trebles the rate. Freezing is known to cause structural damage by ice crystal formation. It seems likely that ice crystals, particularly small intracellular ice crystals formed by very fast freezing rates, enhance the rate of conditioning probably by release of enzymes. Repeated freeze-thaw cycles using relatively low freezing rates does not seem to cause any enhanced tenderizing (James 2002).

For any study where attempts are made to vary the freezing rate, it is important to remember that a range of time–temperature profiles are likely to exist across a sample, and this situation will be exacerbated as the sample size is increased. Therefore, it should not be assumed that changing the external freezing temperature changes the overall rate at which a sample was frozen. However, a study by Doong (1998) indicated that the ice crystal size could be manipulated by changing freezing conditions, and that the ice crystal size correlated with the rate of change of, for example, the water-holding capacity (WHC) of the fillet on subsequent frozen storage. Also, Gonçalves and Ribeiro (2009) suggested that deep or more rapid freezing was more beneficial than slower freezing processes as it was more likely to produce smaller, less damaging ice crystals. A number of papers have also reported distinct advantages in freezing fish using liquid nitrogen (Lee 1982; Gonçalves & Ribeiro 2008a, 2009).

31.2.2 Formation of ice crystals

Freezing involves different factors in the conversion of water into ice: thermodynamic factors that define the position of the system under equilibrium conditions, and kinetic factors that describe the rates at which equilibrium might be approached. The freezing process includes two main stages: (1) the formation of ice crystals (nucleation) and (2) subsequent increase in crystal size (growth). The freezing point of a food may be described as *the temperature at which a minute crystal of ice exists in equilibrium with the surrounding water* (Fellows 2000; Zaritzky 2000).

The rate of ice crystal growth is controlled by the rate of heat transfer for the majority of the freezing plateau. The time taken for the temperature of a food to pass through the critical

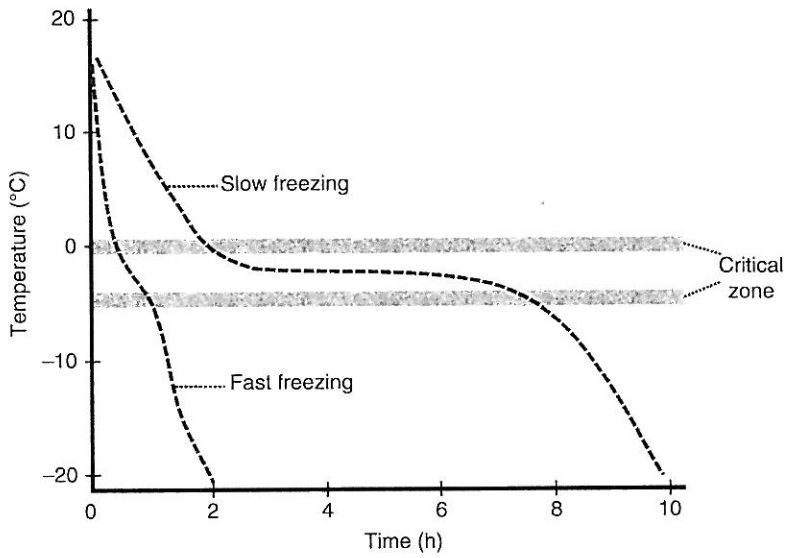

Fig. 31.2 Freezing: temperature changes of food through the critical zone.
Source: Adapted from Fellows (2000).

zone (Fig. 31.2), therefore, determines both the number and the size of ice crystals. The rate of mass transfer (of water molecules moving to the growing crystal and of solutes moving away from the crystal) does not control the rate of crystal growth except toward the end of the freezing period when solutes become more concentrated (Fellows 2000).

Ice formation involves a series of physicochemical modifications that decrease the food quality. The principal physical changes in frozen foods are freeze-cracking, moisture migration, recrystallization of ice, and drip loss during thawing (Zaritzky 2000), where crystals are formed and their size depends on whether the fish is frozen before (pre), during (in), or after (post) rigor mortis (stiffening after death), as well as on how speedy the freezing process is.

In prerigor fish, the water is only inside the muscle cells, and when the fish is frozen, the ice crystals form inside the cells. The ice crystals are mainly small. Large ice crystals form only if the freezing process is slow (e.g., in still air above −18°C). In in-rigor and prerigor fish, a small amount of water, however, remains outside the cells and thus the speed of freezing is significant for the formation of ice crystals. If the freezing is quick, small ice crystals form both inside and outside the cells. However, if freezing is slow, ice crystals first form outside the cells, resulting in an increase in salt concentration. The high salt concentration outside the cells extracts more water from the cells. When this happens, the ice crystals, which have already formed inside the cells, grow in size rather than allowing for the formation of new ice crystals. In in-rigor and postrigor fish, the speed at which the fish are frozen can, therefore, determine how large the ice crystals are and where in the muscle they form. This ranges from many small ice crystals both inside and outside the cells to only very few large ice crystals outside the cells.

Ice crystals form not only during freezing but also during cold storage. Here, not many new crystals are formed, but a recrystallization process takes place in which the surface of crystals, small ice crystals in particular, melts. This melting water subsequently freezes to the larger ice crystals, thereby leading to a greater number of large crystals at the expense of smaller ones. Recrystallization is especially rapid at fluctuating storage temperatures, even when the temperature fluctuates by only a few degrees.

Ice crystals consist of pure water and, therefore, substances that are normally dissolved in the muscle water have less water to be dissolved in as more water is converted into ice. These substances are primarily salts and enzymes, the concentrations of which become very high in the remaining "nonfreezable water." Many of these substances take part in processes that deteriorate the quality of frozen fish. High concentrations of salt, for instance, damage the proteins of the frozen fish. The speed of chemical reactions slows in step with the lowering of the temperature, whereas it accelerates as the concentration of the substances in the reaction increases. Thus, there still are chemical reactions in the "nonfreezable water" at the very low temperatures present in frozen fish due to the very high concentration levels. Reactions take place even at –30°C; however, they are very slow.

31.2.3 Rigor mortis

Immediately after death, the fish muscles are completely lax and the fish feels soft and elastic. When kept in ice, the fish goes into rigor mortis (stiffen) within a few hours. This is because the chemical energy present in the live fish is used up, causing a large part of the proteins in the muscle to bind into a network, which stiffens and hardens the muscle and thus the whole fish. After a couple of days in ice, the fish softens and becomes elastic as certain proteins in the network are broken down by enzymes.

Apart from the physical formation of ice leading to higher concentrations of substances, which in turn speeds up the destructive chemical processes, the ice crystals can directly and physically damage the structure of the muscle. Here, large ice crystals may cause much more damage than the smaller ones. Damage to membranes of muscle cells is particularly serious. This has to do with the fact that some of the cell salts and protein-disintegrating enzymes are in areas confined by membranes. When the membranes are ruptured, the salts are allowed to penetrate into other areas of the cell and increase the chemical processes there.

31.3 FACTORS THAT AFFECT FROZEN FISH QUALITY

31.3.1 Biological parameters

The quality of the frozen product is closely related to the freshness of the raw fish: the fresher the fish before freezing, the better it keeps in frozen storage. Whole fish 3–4 days old in ice show some signs of deterioration on thawing, and the staler the fish the more noticeable are the deteriorative changes that occur on storage. Much fish is now frozen and cold stored pending further processing; this development has been accelerated by the development of freezing at sea on board the fishing vessel (Ranken *et al.* 1997).

31.3.2 Conditions of catching and processing

The conditions of catching and processing are of paramount importance for the deterioration of frozen fish. According to Rehbein (2002), the quality is affected by:

1. *Method of catching, length of trawling time*: affected caloric, moisture, and protein contents, as well as some sensory attributes like muscle firmness.
2. *Stunning and killing procedure*: relationship between killing methods and quality—the more a fish struggles during catch and killing, the faster its pH falls after death. As low pH (~6.0) results in the denaturation of muscle proteins during the frozen storage of fish, the texture may become firm and dry if a stressed fish is processed.

3. *Rigor mortis*: fish can be processed either pre- or postrigor for high-quality products.
4. *Bleeding*: Bleeding the fish carefully prior to processing is beneficial to the quality for two reasons: color and appearance are improved by bleeding, as the presence of blood-stains leads to the devaluation of thawed fillets.
5. *Single and double freezing*: Frozen fillets are prepared directly after the catch on board freezer-trawlers or from fish that has been frozen at sea, transported to a land-based factory, thawed, and filleted. Depending on fish species and processing conditions, small or large differences in quality have been found between single and double-frozen fillets.
6. *Glazing and coating*: glazing protects frozen fillets against freezer burn and lipid oxidation, and edible coatings can reduce the rate of moisture and oxygen transfer between the fish flesh core and the surrounding atmosphere. Battered and breaded fish sticks or fillet portions have a longer shelf life than untreated fillet portions.
7. *Type of product*: the reason for the lower quality and stability is due to the contamination of muscle by blood, kidney, and other tissues that are rich in enzymes and hemeproteins.
8. *Storage conditions*: temperature and time of frozen storage have a large influence on shelf life of frozen stored fish and should be as low as economically possible, but at least less than –20°C.
9. *Freezing and thawing conditions*: it is well known that the speed of freezing has a great effect on the properties of the product. In industry, it is common practice to thaw fish in air or water. More sophisticated techniques, like vacuum thawing, or thawing by the use of microwave, dielectric, or electrical resistance heating, are faster but more expensive.

31.4 THE FREEZE (COLD) CHAIN

31.4.1 Cold storage

The route from catch to consumer is long (Fig. 31.3). Frozen fish products are usually processed in one of two ways: the fish is either frozen aboard the ship or on land. Aboard the ship, the fish is either frozen whole or as fillets. The frozen fillet is often used directly for sale, whereas the whole fish is thawed on land, processed, and then frozen again (double freezing). There is no tradition for double freezing in Danish waters, where the fish is already chilled (stored in ice) and brought on land and subsequently processed and frozen.

Industrial freezing of fish products is done at various stages of production. On board trawlers, whole fish are frozen in vertical plate freezers and fillets in horizontal plate freezers as interleaved fillets or standardized blocks (Bøknæs *et al.* 2001). On shore facilities, the fish are either frozen in blocks for further processing as fish fingers and portions or in retail sizes. The modern fish industry is equipped with quick freezing facilities such as air blast freezers and plate freezers. Fluidized bed and cryogenic freezers are used for individual quick freezing of shrimps and other shellfish. Quick freezing means that the time to pass from 0°C to –5°C must not normally exceed 5–10 h and the warmest part of the product must be the temperature of the following frozen storage room. Due to the flow in production, it is preferable that the total freezing period is no more than 1–2 h. Slow freezing over several days (fish stacked in insulated containers in silent air in a frozen store) can be avoided if the modern equipment is used.

Fish is particularly unstable during frozen storage. There are several reasons for this instability, some of which are more evident in certain fish species than in others. High-fat fish, for example, tend to have a short shelf life in frozen storage due to lipid oxidation, which produces a variety of off-flavors (Reid 1998). Because of the instability of frozen

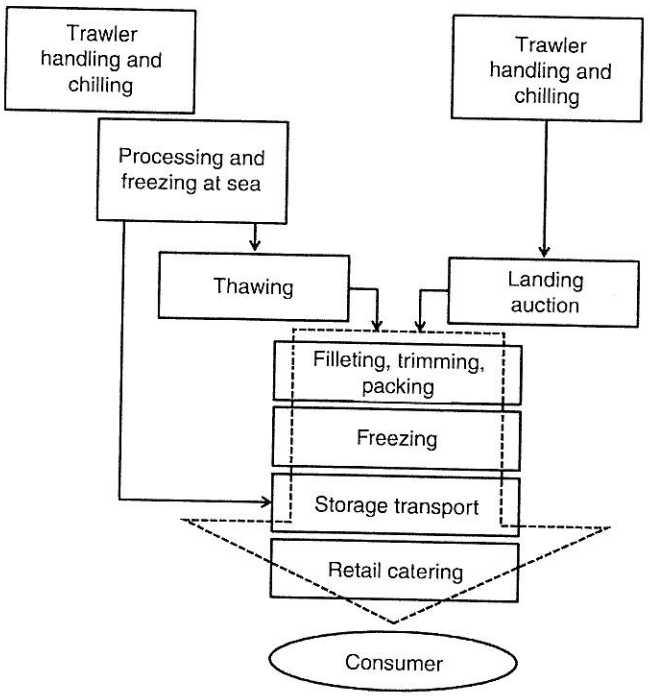

Fig. 31.3 The freeze chain. The fish is either frozen aboard ship or on land.

Table 31.3 Storage stability of frozen fish in days.

Species	−23°C (−10°F)	−18°C (0°F)	−12°C (10°F)
Trout	300	260	110
Cod fillet	300	210	90
Ocean perch	300	220	120
Mackerel	110	80	50
Halibut	350	260	170

Source: From Reid (1998).

fish, it is often recommended that very low storage temperatures be employed. Table 31.3 illustrates the relative frozen storage stability of several species of fish, typical lean fish, fatty fish, and gadoid fish.

The normally recommended air temperature for the storage of frozen foods is −18°C to −20°C. For frozen fish and a few other sensitive foods, the temperature should be much lower, and −30°C is recommended. Even at this temperature, fish do not keep indefinitely. Microbial action ceases below about −10°C, but chemical reactions leading to irreversible changes in odor, flavor, and appearance will slowly continue (Ranken *et al.* 1997). When fish are stored at temperatures above −30°C, deterioration is more rapid and storage life is reduced. Temperatures in distribution vehicles, secondary or distribution cold stores, frozen food rooms, and display cabinets, are all likely to be above −30°C. In some retail display cabinets, they may even be above the recommended level of −18°C. It is important to remember that cold stores are designed to hold frozen goods at the specified temperatures, not to freeze the goods down to those temperatures.

According to the Code of Practice for Fish and Fishery Products (FAO/WHO 2009), the frozen storage facility should be capable of maintaining the temperature of fish at or lower than −18°C, and with minimal temperature fluctuations. Severe fluctuations in storage temperature (more than 3°C) have to be avoided (especially for quick-frozen coated fish products). For frozen fish stored in a trawler, the same control should be done.

It has been suggested that the storage temperature on lean demersal fish should be between −24°C and −30°C. For oily fish, storage temperatures of −30°C to −70°C have been recommended in order to reduce the rate of oxidative changes. However, low-temperature storage is not currently employed, as the cost to the consumer for the final product is too high (Hedges 2002).

31.4.2 Thawing

Ideally frozen fish should be thawed immediately after removal from cold storage. The simplest methods are thawing in still air by simply leaving the frozen product out overnight at room temperature, or thawing whole fish in water. If fillets are thawed in water, they may become waterlogged and lose much of their flavor. For air thawing, the air temperature should not exceed 20°C to minimize bacterial growth on the surface, but very slow thawing must be avoided since bacterial growth may nonetheless cause the outer layers to spoil before the center is fully thawed. Thawing may be accelerated by mechanical means—air blast, heated water, or vacuum methods—or electrically by dielectric resistance or microwave heating. The electrical methods are usually restricted to applications where the size and shape of the units to be thawed are constant, in other words to frozen fish blocks (Ranken *et al.* 1997).

31.4.3 Frozen fish transport

Frozen fish delivered to a destination where they are to be sold immediately are likely to be consumed within a few hours and no harm is done if they are partially thawed on arrival at their destination. The frozen fish may in fact be carried in uninsulated containers depending on how long the journey takes. Enclosed vehicles, however, should be used or at least a cover provided to protect the fish from direct sunlight. An insulated vehicle will be required for long journeys depending on the initial temperature of the fish, whether the vehicle is fully or partly loaded, the size of the load, the insulation quality and thickness, the degree of air ingress, and the local climatic conditions. A local trial will ascertain the maximum range attainable (Johnston *et al.* 1994).

Frozen fish that are to be transferred to other cold stores must be transported in an insulated vehicle preferably with some form of refrigeration equipment to maintain the air space at a temperature of approximately −20°C. The following lists refrigeration methods that may be used: (1) Mechanical refrigeration using either wall coolers or forced convection coolers blowing air throughout the storage space. In some cases, a jacketed system for distributing the air is employed. This is the most common system. (2) Rechargeable eutectic plates. (3) Solid or liquid carbon dioxide or liquid nitrogen can be used with a total loss system (Johnston *et al.* 1994; Gonçalves & Blaha 2010).

During all the transportation steps of the end product, deep-frozen conditions should be maintained at −18°C (maximum fluctuation ±3°C) until the final destination of the product is reached. Cleanliness and suitability of the transport vehicle to carry frozen food products should be examined. Use of temperature-recording devices with the shipment is recommended (Johnston *et al.* 1994; FAO/WHO 2009).

Vehicles should be designed and constructed (1) such that walls, floors, and ceilings, where appropriate, are made of a suitable corrosion-resistant material with smooth, nonabsorbent surfaces. Floors should be adequately drained, where appropriate, (2) with chilling equipment to maintain chilled fish or shellfish during transportation to a temperature as close as possible to 0°C or, for frozen fish, shellfish, and their products, to maintain a temperature of −18°C or less (except for brine frozen fish intended for canning, which may be transported at −9°C or less); (3) so that live fish and shellfish are transported at temperatures tolerable for the species; (4) to provide the fish or shellfish with protection against contamination, exposure to extreme temperatures, and the drying effects of the sun or wind; and (5) to permit the free flow of chilled (Johnston *et al.* 1994; FAO/WHO 2009).

31.4.4 Retail display equipment

Retail display is one of the "weak" links in the frozen food cold chain, mainly due to the contrasting purposes that retail display cabinets have to serve, that is, persuading the customer to buy the product, while at the same time preserving it adequately. For merchandizing purposes, the product must be clearly visible and easy to reach in order to tempt potential customers; however, these features tend toward product temperature fluctuation (i.e., in excess of the recommended −18°C). This is known to be the primary cause of a loss of quality and safety in frozen foods. The best way to protect the product from temperature fluctuations is to keep it as far as possible from the shop environment, and from all possible heat sources (ambient air, lighting, etc.); but this means keeping it out of sight of customers. Matching these two conflicting needs is the main technological challenge facing display cabinet manufacturers (Cortella 2000; Gonçalves & Blaha 2010).

The main characteristics of a good frozen food retail display cabinet can be summarized as follows: (1) it has to guarantee good product temperature control, whatever the external ambient conditions; complying with the standards is crucial in this matter. (2) It has to prove an efficient seller, so the foodstuff must be visible and easily accessible to the customer. (3) It has to be cost-effective, not only in terms of the initial investment, but also in running costs; therefore, its energy consumption is extremely important, but so is easy access for loading, since this reduces the staff hours required to restock the shelves (Gonçalves & Blaha 2010).

While these are the main features of a good frozen food retail display cabinet, nobody—from the manufacturer to the shop managers to their employees—must forget that it is designed neither to freeze food, nor to reduce its temperature: Its purpose is simply to maintain the frozen food at the right temperature. Naturally, the environment where the cabinet is installed plays a major part in establishing how it will behave: Air conditioning and exposure to warm air streams and lighting must be carefully evaluated to guarantee best use of the cabinet (Cortella 2000).

31.4.5 Temperature monitoring

Refrigeration equipment is built to function for long periods without attention; however, there are many events apart from breakdown that can affect temperature control. The defrost cycles need attention to ensure they are at the correct frequency, and loading of food into refrigerated systems is often crucial to its operation and proper air flow. Air temperature monitoring can indicate whether refrigerated equipment is functioning correctly and is being operated correctly, even though it may be more difficult to extrapolate food temperatures. In some circumstances, air temperature monitoring is not possible and product temperature or product simulant temperature is required (Woolfe 2000).

There are an enormous number of different temperature monitoring systems available commercially, from a simple thermometer to a fully computerized system linked to a local refrigeration system or even central control system. The choice of system will depend on exactly the amount of detail the operator requires and the cost at which this information is provided. If the monitoring system is to provide detailed information on the operation of a system linked with other reactive management systems, then obviously a more elaborate and complex system is required. This may include a large number of sensors to enable a very complete picture of the temperature distribution within a refrigerated system to be obtained. It may also include other information such as defrost cycles, compressor and expansion valve pressures, door openings, and energy consumption, and may be linked to an alarm system (and even telephone) stock keeping and batch codes of products. On the other hand, if monitoring is being carried out only to ensure that food is being kept within certain temperatures as a critical control point, then the amount of information that is collected may be reduced (Gonçalves & Blaha 2010).

Temperature monitoring has been discussed in terms of displaying temperature readings of the surrounding air or of the food or simulated food itself. However, it is possible to use a physicochemical mechanism and a resulting color change to display (a) a current temperature, (b) the crossing of a threshold temperature, or (c) an integration of the temperature and the time of exposure to temperature after activation. Such devices are called temperature indicators (TIs) in the first two cases or time–temperature indicators (TTIs) in the last case (Selman 1990; Selman & Ballantyne 1988; Woolfe 2000).

The main causes of loss of storage life are fluctuating temperatures and the type of packaging used. Other factors, including type of raw material, prefreezing treatments, and processing conditions, have a great contribution on frozen seafood quality. Temperature fluctuation has a cumulative effect on food quality and the proportion of PSL or HQL lost can be found by integrating losses over time. Time–temperature tolerance (TTT) and product-processing-packaging (PPP) concepts are used to monitor and control the effects of temperature fluctuations on frozen food quality during production, distribution, and storage (Bogh-Sorensen 1984; Olsson 1984; Evans & James 1993; Ranken *et al.* 1997; Fellows 2000; Woolfe 2000).

Colored indicators are being developed to (1) show the temperature of food (e.g., liquid crystal coatings that change color with storage temperature); (2) indicate temperature abuse (e.g., wax melts and releases a colored dye when an unacceptable increase in temperature occurs); (3) integrate the time–temperature combination that a food has received after packaging; and (4) give an indication of the remaining shelf life (Fig. 31.4) (Gonçalves & Blaha 2010).

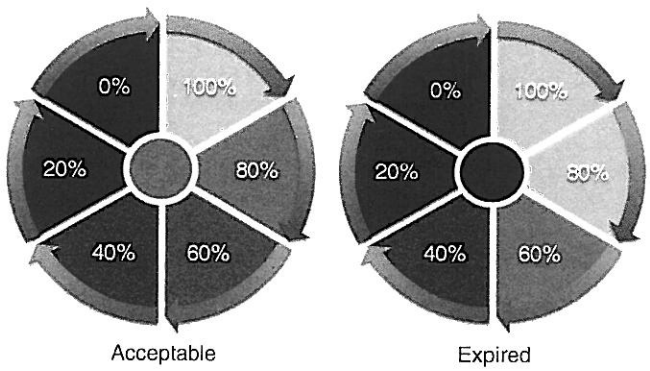

Fig. 31.4 Time–temperature integrator (indicator based on the color change of the inner circle: the percentages show the equivalence of color with the remaining life).

The indicators are normally integrated onto a packaging material that can be attached to the food packaging or the outside of the surrounding or bulk packaging, and can follow the food throughout the chill chain. The type of information that can be provided is one or more of the following: (1) reject or accept on the basis of a color change, (2) temperature abuse above a threshold temperature, (3) partial time–temperature history above a threshold temperature, and (4) full time–temperature history linked to shelf life. Over 100 patents have been filed on processes that could be used as a basis for indicators. These include changes with temperature based on melting-point temperature, enzyme reaction, polymerization, electrochemical corrosion, and liquid crystals. The result of the change is usually a color difference, which can be represented as a static change or moving band. Available temperature and time–temperature devices have been reviewed (Selman 1990; Selman & Ballantyne 1988; Woolfe 2000; Gonçalves & Blaha 2010).

31.5 INDICATORS OF DETERIORATION IN FROZEN FISH

For many years, attempts have been made to determine the shelf life of frozen fish by a number of chemical, biochemical, and physical methods; however, till date the gold standard is sensory assessment by a well-trained panel. Some sensory characteristics of spoilage of frozen fish, together with the reactions they are based on, are summarized in Table 31.4 (Rehbein 2002).

During chilling (i.e., temperatures between 0°C and 5°C), the quality of the fish changes due to oxidation, especially of its fat (oxidative rancidity), self-digestion brought on by the fish's own enzymes (autolysis), and bacterial growth. Normally, the waste products of the bacteria are what cause the fish to smell bad, and bacterial decomposition is what causes its

Table 31.4 Sensory description of thawed cooked fish flesh, and underlying chemical or physical reaction.

Aspect of quality	Underlying chemical or physical reaction
Appearance	
Dry	Protein denaturation
Gaping	Breakdown of connective tissue
Freezer burn	Sublimation of ice
Yellowish	Lipid oxidation; formation of FA
Odor	
Cold-store odor (cardboard)	Formation of carbonyls by lipid oxidation
Sour	Formation of carbonyls by lipid oxidation
Rancid	Formation of carbonyls by lipid oxidation
Amine	TMAO degradation into DMA and TMA
Flavor	
Cold-store flavor	Formation of carbonyls by lipid oxidation
Sour	Formation of carbonyls by lipid oxidation
Rancid	Formation of carbonyls by lipid oxidation
Soapy	Lipolysis
Amine	TMAO degradation into DMA and TMA
Texture	
Dry	Protein denaturation, loss of muscle structure
Firm, tough	Reaction between FA and protein
Soft, mushy	Proteolysis

Source: From Rehbein (2002).

putrefaction. Freezing and cold storage hinders bacterial growth whereas oxidation and autolysis continue, albeit these processes are slowed down when the temperature is below the freezing point. The quality of frozen fish moreover deteriorates because of changes in the structure of proteins (protein denaturation).

31.5.1 The impact of freezing on microorganisms' growth

Frozen foods have an excellent safety record and freezing has never been reported to be the cause of food poisoning. Temperature is one of the major factors affecting microbiological growth. The great advantage of freezing is that microorganisms do not grow in foods when the temperature is −10°C or colder. However, it should not be overlooked that although freezing kills some microorganisms, it does not eliminate pathogenic microorganisms nor microbial toxins present in the food product prior to freezing.

In favorable environments, growth of bacteria normally proceeds as shown in Fig. 31.5, where the logarithm to the number of bacteria is the vertical axis and time is the horizontal axis. First, there is a period of adjustment, the lag phase, where the bacteria are more or less inactive, that is, they do not multiply. The length of the lag time depends on many factors, for example, temperature, pH, inhibitors in the substrate (the food), etc. (Bogh-Sorensen 2000; James 2002). After the lag phase, growth begins and reaches a phase of exponential growth. In the exponential growth phase, the number of bacteria may rise very quickly, often expressed by the generation time, that is, the time required to double the number of bacteria. The generation time varies between bacteria, and depends on several factors, in particular the temperature. The two remaining phases are of less interest (James 2002).

Inactivation of microorganisms caused by freezing and thawing may take place in three ways: (1) When food is cooled so that vegetative microorganisms are kept at temperatures below their minimum for growth, some loss of viability can be expected. (2) Inactivation of microorganisms takes place during the freezing process. The response of microorganisms to freezing is mainly studied in thawed cultures; therefore, the thawing method is a very important aspect that must always be taken into consideration. (3) Finally, inactivation of microorganisms may take place during storage, depending on storage time and temperature.

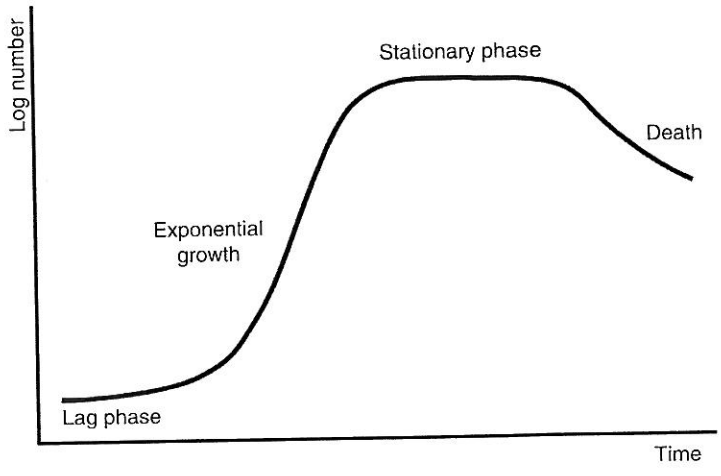

Fig. 31.5 A typical bacterial growth curve.

During the freezing process, the product temperature is lowered and most water in the food is transformed into ice crystals. With decreasing temperature, the liquid phase becomes more and more concentrated. As the volume of ice is about 10% larger than the volume of water, the internal pressure in the food may rise to 10 bar or more, especially during very rapid freezing. Also, during freezing some bacteria are killed, some are in the lag phase, while others may be freeze-damaged (nonlethally injured, sublethally injured). The analytical technique used in microbiological analysis of frozen foods must be modified in order to detect and/or enumerate freeze-damaged cells (Bogh-Sorensen 2000; Jay *et al.* 2005).

Although freezing is a safe preservation method, the food safety issue is still very important. The cold shock response (CSR) could have some implications for frozen foods; often the response is the appearance of cold shock proteins (CSP). The CSR of several microorganisms is being investigated, but comparatively little is known about the response of pathogens to freezing (Kerr 1997). It has been suggested that exposure to stress, for example, freezing, resulting in sublethal injury could render the organism more resistant to the effect of heat, so that heating may not reliably destroy all the bacteria present. Freezing could also result in an increase in the acid tolerance of bacteria, including food-borne pathogens. Another concern regarding the CSR of pathogens is that exposure to low temperatures may have a direct effect on virulence. Kerr (1997) concluded that there is little data in this field, and that further studies of the CSR are clearly required (Bogh-Sorensen 2000).

31.5.2 The impact of freezing on biochemical attributes

As the freezing process converts a large proportion of liquid water into ice, it also concentrates the remaining solution. Enzymes increase the possibility of water being in contact with different substrates. The most common chemical changes that can proceed during freezing and frozen storage are lipid oxidation, enzymatic browning, flavor deterioration, protein denaturation, and degradation of pigments and vitamins. Freezing can give unusual effects on chemical reactions. The temperature and concentration of the reactants in the unfrozen phase (freeze concentration effects) are the main factors responsible for changes in the reaction rates of enzymatic and nonenzymatic reactions during freezing. The formation of ice crystals can produce the release of enclosed contents in food tissues (enzymes and chemical substances) affecting the product during freezing and storage, leading to quality deterioration.

31.5.2.1 Fat and fat decomposition

Fish contain fat, and changes in the fat fraction of fish greatly influence the taste of the frozen product. The amount of fat in the muscle of fish varies from species to species, and great variation may occur even within the same species, for example, in the herring where the content of fat may vary from 1% to 22% in 1 year. The fat content of fish can vary from 0.2% to around 25%.

The fat or lipid content of fish is found in the membranes of cells and as lipid depots just under the skin, in the belly flap, and in the connective tissue. Membrane lipids (primarily phospholipids) make up less than 1% of the total lipid content. Membrane lipids and the fat in lipid depots (primarily triglycerides) consist of long fatty acids. During freezing, the fat decomposes and is converted into substances that taste unpleasant. The changes are due to oxidation or enzymatic degradation.

Fish fat has a particularly high content of polyunsaturated fatty acids, especially susceptible to oxidation, which produces aldehydes and ketones that have a rancid flavor and odor.

Enzymatic and nonenzymatic pathways can initiate lipid oxidation. One of the enzymes that is considered important in lipid oxidation is lipoxygenase, which catalyses the addition of molecular oxygen to a cic-cis-4 pentadiene containing unsaturated fatty acid, releasing a stereo-specific conjugated diene hydroperoxy fatty acid product.

31.5.2.2 Oxidative rancidity

The development of rancidity can still occur quite rapidly even in the frozen state (Ortiz & Bello 1992). The rate of rancidity development once frozen may also be influenced by a number of enzymatic and nonenzymatic events occurring prior to freezing (Haard 1994). In the living muscle, the effects of agents that accelerate lipid oxidation (prooxidants) are balanced by those that inhibit oxidation (antioxidants). Postmortem, however, this balance is disrupted and stimulates the initiation of lipid oxidation. In fresh fillets stored at chill temperature, off-flavor development is less problematic since microbial spoilage will render fish inedible before rancidity has developed to any great extent. However, in the frozen state, where microbial-induced changes are effectively arrested, rancidity is most likely to become the process that limits the shelf life of fatty fish in particular (Harris & Tall 1994).

Oxidation takes place on the surface of the fish, and smaller fish such as mackerel and herring with a relatively large surface go rancid more rapidly than other fish. The cleaning and cutting into filleting of fish increases the total surface area, and the fish therefore become more rancid. Oxidation often takes place very soon after the fish has been killed, especially in the fat layer just under the skin. Moreover, the process is exacerbated by salt and metals such as iron from, for example, the blood of the fish. In codfish, oxidative lipid degradation may give poor flavor, namely, the very characteristic cold-store flavor (due to the substance cis-4-heptenal). Thus, the occurrence of lipid oxidation in frozen foods leads to loss of quality: flavor, appearance, nutritional value, and protein functionality. Decomposition of hydroperoxides of fatty acids to aldehydes and ketones is responsible for the characteristic flavors and aromas known as rancidity.

31.5.2.3 Can oxidative rancidity be avoided?

Oxidative rancidity in frozen fish can be avoided, or at least counteracted, in several ways. First of all, the fish must be frozen as quickly as possible after death, however, allowing time for proper bleeding of the fish in ice water. As mentioned, oxidative rancidity is an oxygen-dependent surface process; glazing and vacuum packing, which reduce the degree of contact with oxygen, are therefore advantageous.

31.5.2.4 Protein changes

In lean fish, protein changes have the greatest influence on the shelf life of the frozen and cold-stored fish. The main causes of freeze-induced damage to proteins are ice formation and recrystallization, dehydration, salt concentration, oxidation, changes in lipid groups, and the release of certain cellular metabolites. Freeze-induced protein denaturation and related functionality losses are commonly observed in frozen fish, meat and poultry. Losses in functional properties of proteins are commonly analyzed by comparing the WHC, viscosity, gelation, emulsification, foaming, and whipping properties. Freeze-induced protein denaturation is often attributed to the formation of ice crystals, dehydration, and the concentration of solutes in the tissue or protein solution. Freezing has an important effect in decreasing the WHC of muscle systems on thawing. This decrease occurs during freezing,

Table 31.5 Enzymes tested as an indicator of quality of frozen fish.

Enzyme	Activity
Myofibrillar ATPase	Drop in activity was not correlated with protein solubility or toughness
Aldolase	Decline in soluble enzyme activity observed for cod and haddock stored at −14°C
Malic enzyme (ME)	Latent form of ME showed a decrease in activity when fish was stored for 5 months at −7°C, but no change at −29°C
Alpha-glycerophosphate dehydrogenase	The test, determination of activity constant from a double reciprocal plot of reaction velocity, was very time consuming
Sarcoplasmic ATPase	Rapid decrease during frozen storage
Cytochrome oxidase	Activity decreased during frozen storage of cod and it was possible to distinguish between frozen storage temperatures −9°C, −20°C, and −40°C
Acid phosphatase	Activity decreased during frozen storage of cod at −30°C
50-Nucleotidase	Activity decreased during frozen storage of cod at −30°C
Phospholipase	Activity increased in the 1st weeks of frozen storage of cod at −30°C, then it declined to reach the original level

Source: From Rehbein (2002).

because water–protein associations are replaced by protein–protein associations or other interactions.

When thawing, plenty of water drains from the fish (drip loss), and the fish becomes less juicy and less suitable for minced fish meat products. Protein changes also affect flavor. Proteins may, in their natural structure, bind undesirable flavors that are released during freezing. Oxidative reactions such as lipid peroxidation are also involved in the deterioration of functional attributes of muscle proteins during frozen storage (Zaritzky 2000).

Protein denaturation in frozen fish should be accompanied by a decrease of enzyme activities. Therefore, a number of enzymes (Table 31.5) have been tested for a regular disappearance of activity during frozen storage. Recently, the activity of cytochrome oxidase, an enzyme located in the inner mitochondrial membrane, was measured in the muscle of fresh and frozen cod (*Gadus morhua*). Activity was enhanced by freezing, and then declined during the frozen storage depending on the temperature (Godiksen & Jessen 2001; Rehbein 2002). The authors conclude that cytochrome b may have potential as an indicator of frozen storage conditions. Release of particle-bound enzymes due to freezing and thawing has been used for differentiation between fresh and frozen fish. Mitochondrial (3-Hydroxyacyl-CoA dehydrogenase [HADH], Glutamate-Oxaloacetate transaminase [GOT], malic enzyme [ME], fumarase) as well as lysosomal enzymes (acid alpha glucosidase, beta-*N*-acetylglucosaminidase) were found to be suitable depending on the fish species.

In frozen gadoid fish, the TMAOase catalyzed the production of formaldehyde (FA), and dimethylamine (DMA) from trimethylamine oxide (TMAO) occurs at temperatures down to −30°C. Both metabolites, which are formed in equimolar amounts from TMAO, can be used as parameters for the deterioration of frozen fish, as the binding of FA to proteins was found to result in texture toughening (Rehbein 2002). During TMAO degradation, small amounts of FA are formed, which apparently bind the proteins and thus make them less able to bind water.

In frozen fish, the degradation of adenosine triphosphate (ATP) and related nucleotides occurs mainly in the temperature range between −5°C and −15°C, and was found to be very slow at lower temperatures. Therefore, the determination of adenosine monophosphate (AMP), inosine monophosphate (IMP), or hypoxanthine has not been applied very much for the quality measurement of frozen fish (Rehbein 2002).

Changes of proteins in fish meat during freezing and cold storage may be also examined and monitored via proteome analysis, a relatively new technique for examination of the protein composition in cells and tissues, such as fish muscle.

31.5.2.5 Can protein changes be avoided?

It is relatively simple to hinder protein changes in frozen fish. Processing the raw material shortly after catching, quick freezing, and cold storage at a low and stable temperature will reduce protein denaturation significantly.

31.5.3 The impact of freezing on sensory attributes

While a number of characteristics affect the overall quality and acceptability of both fresh and frozen meats, tenderness is the major characteristic of eating quality because it determines the ease with which meat can be chewed and swallowed. The tenderness of meat is affected by both chilling/freezing and storage. Under the proper conditions, tenderness is well maintained throughout the chilled/frozen storage life, but improper chilling/freezing can produce severe toughening and meat of poor eating quality (James 2002).

During the freezing and subsequent frozen storage of certain fish species, changes occur that result in the deterioration of the textural quality of the cooked fillet. The textural change has been described as a tendency to express liquid on initial compression in the mouth, with the remaining material being often hard, dry, and fibrous.

The textural changes that occur have been attributed to changes in the myofibrils. Many observations of myofibrillar change have been made; for example, work by Jarenback and Liljemark (1975) showed that during the frozen deterioration of cod (*Gadus morhua*), a decrease in the dimensions of the myosin lattice was observed, coupled with disturbances to the regular hexagonal lattice spacing (based on a comparison of thawed, deteriorated muscle with fresh cod). It was also noted that the myofibrils within a thawed, frozen, deteriorated muscle fiber were pushed closer together, with a commensurate disappearance of the sarcoplasmic reticulum vesicles lying between the myofibrils. Similar effects have also been reported for the *Alaska pollock* muscle that had been subjected to −20°C frozen storage for 2 months. On thawing, the myofibrils within each muscle cell did not recover their original diameter, and also appeared closer together. Further frozen storage (i.e., 12 months at −20°C) rendered the myofibrils even less able to effect a recovery of their original diameters on thawing, and a substantial loss of the order within individual myofibrils was also observed (Hedges & Nielsen 2000).

Although textural change may be significant during the storage of cod and *Alaska pollock*, flavor changes may also occur. One flavor change is often described as the development of cold-store flavor and has been attributed to the development of hept-cis-4-enal, a product of oxidation of specific membrane phospholipids (McGill *et al.* 1977). It has also been suggested that starving cod prior to slaughter reduces the development of off-flavors (Ross & Love 1979; Hedges & Nielsen, 2000).

The appearance of meat at its point of sale is the most important quality attribute governing its purchase. The ratio of fat to lean and the amount of marbled fat are important appearance factors and another is the color of the meat. The changes in the color of the muscle and blood pigments (myoglobin and hemoglobin, respectively) determine the attractiveness of fresh red fish meat, which in turn influences the consumers' acceptance of meat products. Consumers prefer bright red fresh meats, brown or gray-colored cooked meats, and pink cured meats. The color red is more stable at lower temperatures because the rate of oxidation of the pigment

decreases. The color of frozen meat varies with the rate of freezing. Those frozen at −34°C to −40°C had the most desirable color and those frozen at −73°C to −87°C tended to be pale (James 2002). At low temperatures, the solubility of oxygen is greater and oxygen-consuming reactions are slowed down. There is a greater penetration of oxygen into the meat and the meat is redder than at high temperatures.

31.5.3.1 How can changes in sensory quality of frozen fish be seen?

The quality of a frozen fish depends on its initial quality and on how it is handled. A white fish such as a cod is cleaned and bled immediately after being killed. This means that the guts are removed and the blood is allowed to drain from the muscles. In an entirely fresh cod, the blood has no effect on quality. However, when the fish is frozen and kept in cold storage, the blood may give the fish a metallic tinge and later contribute to its going rancid. When a lean fish such as cod goes rancid, it will often taste somewhat like wet cardboard (cold-storage flavor). Fatty fish such as salmon and herring do not acquire a cold-storage flavor but will acquire a rancid flavor of cod liver oil if not properly protected in airtight packaging during storage.

31.5.3.2 Differences in the freezing quality of fish populations belonging to the same fish species

Different batches of cold-stored cod can be of very different quality even though the fish were handled identically and stored in the same period of time. This could be due to differences in the composition of the fish, which changes, for example, depending on the time of season and spawning. Researchers believe the reason lies in both hereditary and environmental conditions.

- *Hereditary differences* can occur when a cod in a certain location acts like an individual population, not particularly interested in mixing with cod from another location (belonging to another population). Hereditary differences will be seen between such populations.
- *Environmental differences* can occur when cod from a population stay in two different locations, where conditions differ so that the fish develop differently.

The interplay between the hereditary genes of the individual and its environment defines its "appearance" (size, shape, chemical composition, etc.), in other words it defines the phenotype of the individual fish. A fish product manufactured from several different phenotypes may vary in quality even though the fish were handled identically aboard the fishing boat and at the factory.

If cod is handled with care during and after catching, if it is frozen as quickly as possible and stored at a stable temperature of −30°C (or below), there will be no difference in taste between a thawed and a fresh fish for the first month. After 3 months, rancidity sets in, cold-storage flavor starts to develop, and the taste characteristics of the specific species gradually disappear completely. However, the frozen fish may be suitable for consumption for up to 1 year when kept in cold storage at a low and stable temperature.

Fatty fish, especially large fish like salmon, are more suitable for freezing than cod and at low temperatures may be suitable for consumption for up to 1.5 years (Sørensen *et al.* 1996).

Also here, the taste of the fish becomes more and more neutral; however, off-flavors will only develop after very long storage times, and rancidity occurs only if the fish has not been packed properly.

Numerous consumer studies show that retailed frozen fish taste significantly poorer than fresh fish. As a consumer, you can never be sure of the quality of the fish you buy—there is nothing on the packet to indicate the quality of the fish. Packets are labeled with the packaging date, but say nothing about when the fish was caught, the temperature at which it has been stored, for how long it has been stored as raw material, or if it has been frozen and thawed several times, etc.

The consumer evaluates the eating quality of a fish through the senses—by the look, smell, texture, and taste of the fish—using sensory assessment. As only the consumer can determine what he or she likes, such an evaluation will be subjective. Sensory assessment may also be applied professionally, by individuals who have been trained in the assessment of specific properties of fish. In this way, sensory assessment becomes objective. To handle the quality of fish through the frozen fish chain, the quality index method (QIM) has proven to be a good tool for frozen cod (Warm *et al.* 1998; Jensen *et al.* 2001).

The QIM for frozen fish can be looked upon as a simple profile. Tables 31.6 through 31.9 show the schemes developed for frozen cod from raw material to product.

For frozen fish, the theoretical demerit line (see Chapter 29) has been more difficult to determine than the one for fresh fish because of the extended storage time dependent on the freezing method, temperature of frozen storage, temperature fluctuations, etc. The approach for establishing a quality index for frozen fish (cod) has, therefore, been different from the method used for fresh fish. The decision of which parameters to choose in the QIM schemes for frozen cod was based on parameters for fresh cod showing the largest variation over time. The goal with the development process was to describe each score in a way so that people with little training in sensory assessment of fish understood the description. This required a

Table 31.6 QIM scheme for thawed whole cod.

Quality parameter	Characteristics
Texture	0: Firm texture. Stiff and firm to finger touch 1: Elastic to finger touch. Marks disappear after a few seconds 2: Fairly soft and plastic flesh. Marks do not disappear 3: Very soft. The flesh is easily penetrated on pressure
Remains of guts	0: No remains in the belly 1: Few remains in the belly 2: Many remains in the belly
Shape of fish	0: Normal round shape as freshly caught cod 1: Fairly normal round shape with few marks after freezing 2: Very mechanically damaged during freezing. Very deformed
Marks from fishing tackles/catch handling	0: No marks 1: A few small marks 2: Many marks 3: Very many/big marks
Odor	0: Fresh marine and seaweedy 1: Neutral 2: Slightly sour and metallic 3: Strong sour and metallic. Painty
Appearance	0: Iridescent or opalescent. Bright, shining. No bleaching 1: Slight bleaching 2: Dull and very bleached, no iridescent. Freeze dried
Flesh color in open spaces	0: Open surfaces white and blood in throat cut red 1: Open surfaces gray or slightly yellow 2: Open surfaces yellow or brown 3: Open surfaces very yellow and brown. Milky surfaces as freeze dried

Table 31.7 QIM scheme for thawed fillet.

Quality parameter	Characteristics
Texture	0: Firm and stiff texture. No wateriness 1: Slightly soft, initial wateriness 2: Soft, wateriness noticeable 3: Very soft and pronounced wateriness
Odor	0: Neutral 1: Slightly sour off-odor 2: Very sour off-odor
Color	0: Plain white 1: Grayish 2: Gray, starting yellow maybe slightly red 3: Either yellow or very red. Milky surfaces as freeze dried
Blood stains	0: No stains 1: A single stain (diameter less than 3 mm) 2: Single small stains (1–2 with a diameter under 5 mm) 3: Very discolored from many stains or totally red
Gapping	0: No gapping, coherent 1: Slight gapping 2: Gapping noticeable, disrupted 3: Gapping pronounced, disrupted
Parasites	0: No parasites 1: One parasite 2: More than one parasite

Table 31.8 QIM scheme for cooked fillet from thawed cod.

Quality parameter	Characteristics
Odor	0: Sweet, marine, and seaweedy 1: Loss of odor 2: Neutral 3: Slightly cold-storage odor (cardboard), slightly citric, amine 4: Cold-storage odor (cardboard), citric, strong amine
Color	0: White and opalescent 1: Loss of whiteness 2: Grayish, one small blood stain 3: Slightly yellow, a few small blood stains 4: Light brown. Discolored of blood
Flavor	0: Sweet, marine, and seaweedy 1: Loss of taste, slightly sweet 2: Neutral 3: Slightly cold-storage flavor (cardboard), insipid, slightly as soap, slightly citric, slightly amine 4: Cold-storage flavor (cardboard), dry fish, soap, citric, strong amine
Texture	0: Very succulent, flaky, and coherent also succulent after chewing several times 1: Succulent, flaky, and coherent. Succulent after chewing several times 2: Initial feeling is succulent, watery after first chewing. Dry and tough during following chewings 3: Dry, fibrous, and/or tough. Dry and tough from the first chewing 4: Very dry, fibrous, and/or tough. Very tough from the first chewing

Table 31.9 G

Category
High quality: Inc
Medium quality: Quality index 5-
Low quality: Quality index 1

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Table 31.9 QIM score—use of product.

Category	Examples of characteristics	Use of product
High quality: Index 0–4	• Firm texture • Neutral odor • White color • No blood stains • Minimum gapping • No parasites	• Many possibilities for use • Luxury products (loins, tails, etc.)
Medium quality: Quality index 5–12	• A little soft and watery • Somewhat sour odor • Grayish color • Single blood stains • Medium gapping • One parasite	• Breaded products • Several cuttings • Block products
Low quality: Quality index 13–16	• Very soft, very dry • Very sour odor • Yellowish, reddish • Big blood stains • Much gapping • More than one parasite	• Very few possibilities for use • Block products

difference between each score. Ranking the descriptions for each parameter and giving numbers to the ranks in succession from 0 to 4, the indexing method has been established for whole fish, fillets, and cooked fillets. The grading schemes have been evaluated and further developed in a great number of trials by both trained and untrained panel members using frozen cod from the Baltic Sea, Iceland, and Russia. The different parameters have been assessed and the parameters selected to give a picture of the total sensory quality.

A manual containing the total plan for evaluation, explanation of the evaluation terms, and color slides illustrating the different levels of quality of frozen cod and cod fillet has been produced for industrial use.

The three QIM schemes can be used effectively through the chain from fisherman to consumer. It will be possible to check out critical points in a production line by the QIM. When the quality index differs significantly from whole fish to fillet, a decision can be made to change the production conditions. A continuous problem about QIM is the setup of various quality categories. For thawed fillets, three categories were suggested (Warm 2001), as shown in Table 31.9.

An advantage of the QIM is that the limits for quality categories can be set individually depending on the product.

31.5.4 The impact of freezing on physical attributes

Weight may be lost by dehydration or due to physical damage of the fish during the freezing process. Physical damage may be due to damage during freezing, which results in small pieces being broken off; this is likely, for instance, in freezers where the product is fluidized by the cooling air. The other form of physical damage encountered during the freezing process is due to fish adhering to trays or conveyor belts. If the weight loss on releasing fish from trays is excessive, the trays may be sprayed on the underside with water to assist release. Fish frozen in continuous freezers with stainless steel link or mesh belts may stiffer weight losses due to small particles being trapped in the belt. Losses due to physical damage in a freezer should be

small and need not be more than about 1% if the freezer and freezing process is suitable for the product (Johnston *et al.* 1994; Campañone *et al.* 2001).

Weight loss due to dehydration in a freezer depends on a number of factors, and the weight losses in air blast freezers give rise to the greatest controversy. Weight loss due to dehydration will depend on the (1) type of freezer, (2) freezing time, (3) type of product (food surface), (4) air velocity, (5) freezer operating conditions, and (6) during storage (room temperature fluctuations) (Gonçalves & Blaha 2010).

The denaturation of fish muscle proteins during frozen storage leads to a decreased water-binding capacity (WBC), and a dry, firm, and tough texture, if the time–temperature profile of storage is unfavorable. The state of water in frozen-thawed fish has been determined as thaw drip (TD), WHC, WBC, or cooking loss (CL). The amount of water released during thawing (TD) can be used as a simple method to get initial information on the properties of the product. WHC was determined in most experiments to describe protein–water interaction during the frozen storage of fish. Some examples are compiled in Table 31.10 showing the suitability for the technique for quality assessment and the shelf life determination of frozen fish (Rehbein 2002).

During freezing, pure water is separated from the system in the form of ice crystals. Solute concentration increases and melting temperature decreases following the thermodynamic equilibrium line. Freezing can also be considered as a dehydration process in which frozen water is removed from the original location in the foodstuff and forms ice crystals. During thawing, water may not be reabsorbed in the original regions, leading to the formation of drip. Factors that affect drip losses are size and location of ice crystals, rate of thawing, the extent of water reabsorption, the status of the tissue before freezing, and the WHC of the tissue (Zaritzky 2000).

Freezing does not stop weight loss. After meat is frozen, sublimation of ice from the surface occurs. If the degree of sublimation is excessive, the surface of the meat becomes dry and spongy, a phenomenon called "freezer burn." Developments in the use of moisture impervious packaging materials have significantly reduced sublimation in frozen meat (James 2002).

Much has yet to be done to correlate the rate of weight loss with differences between storage conditions, but the rate of weight loss has been shown to vary with the following: (1) temperature, (2) temperature fluctuation, (3) humidity, (4) heat transfer, (5) air flow over the product, (6) radiation effects of lighting, (7) the product, (8) shape and size of the product, and (9) type of wrapper (Gonçalves & Blaha 2010).

Table 31.10 Water-holding capacity of frozen and thawed fish.

Fish species and type of product	Storage conditions	Results
Whole cod (*Gadus morhua*)	Different combinations of time and temperature	WHC was strongly negatively correlated with the chemical quality parameters DMA and FA
Fillets of Argentine hake (*Merluccius hubbsi*)	7 weeks at −7°C	WHC was affected by sex, size, and sexual maturity of the fish
Blue crab meat (*Callinectes sapidus*)	32 weeks at −29°C	WHC was improved by cryoprotectants
Single- and double-frozen fillets of cod (*Gadus morhua*)	9 months at −22°C	WHC decreased considerably during storage of double-frozen fillets, but only slightly for single-frozen fillets
Minced prawn flesh (*Penaeus* spp.)	90 days at −12°C	Initial WHC was very high; the slight decline during freezing was diminished by cryoprotectants

Source: From Rehbein (2002).

Most codes of practice only state the temperature for storage. Variations in the other factors that control the rate of dehydration can, therefore, result in cold stores having widely different storage conditions. The rate at which the product loses weight by dehydration can, therefore, vary considerably. There are great differences between the quality of cold stores that may be attributed both to their design and mode of operation as well as to the operating temperature (Johnston *et al.* 1994).

The rate of weight loss within a store can vary considerably with location. Fish stored near fan coolers, where they are subjected to high air velocities, will quickly show signs of dehydration. Fish stored against walls remote from the cooler may be subject to poor air distribution and heat gains from the store walls. This can cause temperature fluctuations in the product, which inevitably results in high dehydration losses (Gonçalves & Blaha 2010).

Storage and transport conditions have a great influence on the quality of frozen foods. Ice recrystallization can be defined as the increase of the average size of the ice crystals. The driving force for this phenomenon is the difference in the surface energy of two adjacent crystals, this energy being proportional to the crystal curvature. Recrystallization reduces the advantages of fast freezing, inducing physicochemical changes that alter product quality. There is a direct relationship between crystal size and the number of faces the crystal has. Small crystals with three or four faces show concave surfaces, and tend to disappear because the limit of the crystal migrates toward the center of the curvature. Six-sided crystals have plane surfaces and are stable, and those with a higher number of faces tend toward growth. Crystal growth occurs at a constant temperature but is accelerated by fluctuations and thermal steps (Zaritzky 2000).

Concepts like dehydration increase of the ionic strength and concentration gradients can be applied to recrystallization. In the course of freezing and storage, each crystal is surrounded by a saline solution of a determined concentration. The increase in ice crystal diameter during recrystallization leads to a redistribution of this solution around the tissue; its interaction with the protein structure contributes to denaturation, which also produces an increase of the exudate released by the tissue after thawing. Temperature fluctuations accelerate the rate of recrystallization. As temperature increases, the small ice crystals melt. Then when the temperature decreases again, since new nuclei cannot be formed, water is converted into ice on the existing crystals, hence increasing their size (Martino & Zaritzky 1987, 1988, 1989; Zaritzky 2000).

The thawing process must be conducted with care if quality and yield are to be preserved. Regardless of the selected procedure, energy must be provided to melt the ice. Thawing must be designed in order to minimize microbial growth, water release, evaporation losses, and deteriorative reactions. Thawing requires longer times than freezing for comparable temperature driving forces. This is because during thawing the heat is transferred through the unfrozen zone of the foodstuff where thermal conductivity is lower than that of the frozen zone. With regard to exudates production, in frozen meats a slow thawing process at low temperatures is sometimes recommended to permit water diffusion in the thawed tissue and its relocation in the fibers (Zaritzky 2000).

31.6 SAFETY AND QUALITY ASSURANCE FOR FROZEN FISH

31.6.1 Frozen supply chain

Fig. 31.6 shows a simplified fish supply chain, going from catch through to the retail cabinet. The main factors that determine frozen fish quality can be grouped into three main areas: prefreezing, the freezing process, and frozen storage/product distribution. It should also be

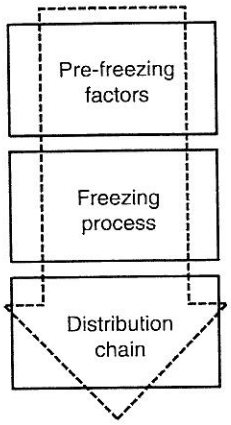

Fig. 31.6 A simplified diagram of key stages in the supply chain for frozen fish products.
Source: Adapted from Hedges and Nielsen (2000).

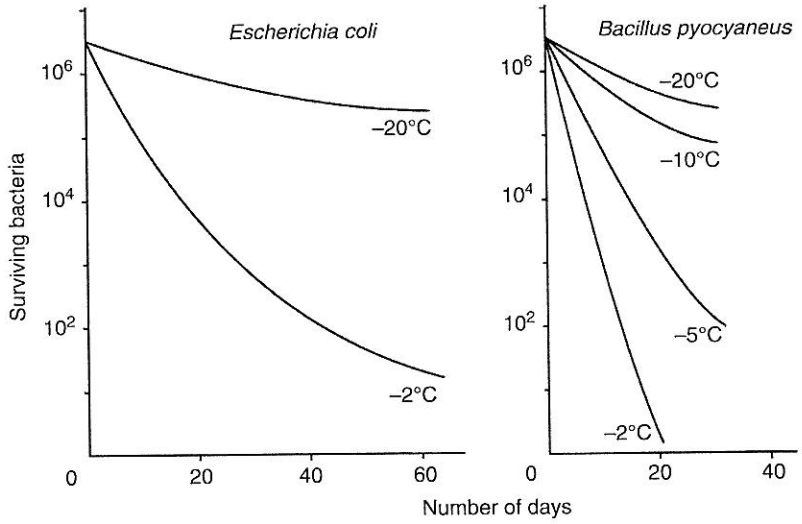

Fig. 31.7 Number of bacteria during storage at different temperatures. The bacteria were frozen to an end temperature of −70°C.
Source: Adapted from Bogh-Sorensen (2000).

borne in mind that one of the least well-defined areas in any supply chain is the consumer handling stage, and it is during this phase that potentially severe thermal abuse may occur. Indeed, thermal abuse may not be confined to the frozen state but may extend to poor cooking of products also (Hedges & Nielsen 2000).

In practice, foods are frozen to be stored for a certain period, often several months. Frozen storage is always included, and it is the combined effect of the freezing (and thawing) process and frozen storage that is of interest. When counting microorganisms in frozen foods during storage at different temperatures, the result is often as shown in Fig. 31.7. Warm storage, that is, temperatures greater than −8°C, results in much larger inactivation of microorganisms than storage at −18°C or less. Freezing and storage at very low temperatures, down to −150°C or even less, seems to result in increasing survival.

During frozen storage, the above-mentioned mechanisms (cell dehydration, membrane damage, etc.) continue to act upon the microorganisms, eventually leading to injury or death of a certain part of the organisms. It is also suggested that the death of microorganisms may be caused by long-time exposure to concentrated solutions, both internal and external. The inevitable temperature fluctuations in the cold chain cause the recrystallization of ice crystals, increasing the salt concentration as well as the damage to microorganisms. The increasing size of the ice crystals during storage reduces the difference between foods frozen very rapidly and foods frozen with a normal freezing rate, and have some influence on the survival of microorganisms (Bogh-Sorensen 2000; Gonçalves & Ribeiro 2009).

31.6.2 Prefreezing factors influencing storage stability

Freezing and cold storage is an efficient method of fish preservation, but it must be emphasized that it does not improve product quality. The final quality depends on the quality of the fish at the time of freezing as well as other factors during handling, prechilling, freezing, cold storage, and distribution. The important requirement is that the fish should at all times be kept in a cool condition before freezing, about 0°C, and the use of ice or other methods of chilling is recommended. Apart from keeping the product chilled, it is also essential to adopt a high standard of hygiene during handling and processing to prevent bacterial contamination and spoilage. In some countries, chemicals are currently used to treat fresh fish in order to assist with such things as color retention and the retention, or even addition, of fluids. The treatment of food with chemicals is usually subject to national and local restrictions and it would be inappropriate to make any general comment on their use in this document (Gonçalves & Blaha 2010).

Clearly, in any fish product supply chain there are many points at which improvements may be made. However, to obtain real benefits the supply chain must be viewed in its entirety. Thus, there may be little to be gained by controlling the quality of raw materials if inappropriate freezing and storage conditions are employed during processing and distribution.

Product preparation has a considerable effect on quality. It is better to eviscerate fish before they are frozen since blood and kidney tissue can be removed. Blood contains iron, a cofactor for TMAOase activity, and kidney remnants may contain proteolytic enzymes that will degrade the fillet structure. Whole fish have longer shelf stability than fillets, which are more stable than minces. This increasing instability, which is more apparent in white fish, probably results from the release of salts and enzymes due to tissue damage, which then leads to more rapid deterioration. Also, the mixing of red and white muscles (red muscle containing more fat and more hem proteins) may result in the dispersion of lipids and enzymes, leading to more deteriorative changes (Gonçalves & Blaha 2010; Gonçalves 2011).

According to Hedges and Nielsen (2000) and Gonçalves and Blaha (2010), many parameters affect the shelf life of fish and the main prefreezing factors are listed as follows:

1. *Fish type*: fish of different types spoil at different rates. In general, it can be stated that larger fish spoil more slowly than small fish, flat fish keep better than round fish (Kim *et al.* 1977), lean fish keep longer than fatty fish (under aerobic storage), and bony fish are edible for longer periods than cartilaginous fish.
2. *Handling*: Rough handling will result in a faster spoilage rate. This is due to the physical damage to the cells of the fish, resulting in easy access for enzymes and spoilage bacteria. Also, rough handling may lead to damage/bruising, which may accelerate deteriorative processes. If fish are kept alive in containers until processing and freezing, microbial spoilage can be avoided. The fish are, however, starved under these conditions

and use up glycogen. Thus, as with catching and handling procedures that cause energy stored to become depleted before death, the pH of the muscle tends to be higher.

3. *Effect of postmortem pH*: The postrigor pH varies between fish species but is generally higher than in meat from warm-blooded animals. The catching method (Botta *et al.* 1987), handling prior to death, time of year, and fishing ground may all influence the final pH of the fish fillet (Love 1975a, b). The ultimate pH of the fish fillet has a direct effect on the WHC of the muscle and on the fish texture. The pH of the muscle influences the shelf life of fish stored on ice, where the shelf life increases with a decreasing pH. The final pH may also influence the properties of the connective tissue, and especially the propensity for fillets to gape (Love and Haq 1970). Gaping is a phenomenon whereby the connective tissue is unable to hold the muscle blocks together.
4. *Prechilling*: The postcatch and postmortem handling of fish is different from that of meat, even though they are both usually chilled. Fish temperature reduction to about 0°C is by far the most important factor for the quality of fish. This should be achieved as rapidly as possible. Traditionally, ice is used in the prechilling of fish. This has several advantages. The first one is that the ice and fish are in good contact, allowing good heat transfer from the fish to the ice. The second is that the melting of the surrounding ice requires a large amount of heat energy to be removed from the fish. The disadvantage with icing is that it can be labor intensive, and for fish in boxes, the contact between the fish and ice may not be very good. Rapid chilling will slow down the rates of enzymatic- (and microbial-) induced changes occurring postmortem. Of these postmortem changes, the earliest ones observed by trained sensory panelists are those that relate to changes in appearance and texture. The most dramatic change is the onset of rigor mortis. The rate of onset and resolution of rigor varies from species to species and is affected by temperature, handling, size, and physical condition of the fish. Indeed, for farmed salmon it has been shown that stress prior to slaughter can influence the speed of rigor development and the textural quality of the fillets. Fish may also be cooled in refrigerated sea water. This allows faster heat removal from the fish and speeds up the chilling process (super chilling). Also, the temperature of the fish can be reduced from −1°C to −2°C, and this may offer advantages in reducing rates of spoilage. An extension to super chilling is to allow the fish to freeze partially. By reducing the temperature of the fish from −2°C to −4°C, fish can be partially frozen. It has been claimed that such partial freezing of fish can extend shelf life. This may offer advantages for preserving fish quality on board trawlers that do not freeze fish at sea (Gonçalves & Blaha 2010).
5. *Addition of cryoprotectants*: compounds that improve the quality and extend the shelf life of frozen foods. A wide variety of cryoprotective compounds are available, and these include sugars, amino acids, polyols, methyl amines, carbohydrates, some proteins, and inorganic salts such as potassium phosphates and ammonium sulfate. The selection of cryoprotectants will depend on whether the application is for a comminuted product, that is, a system into which the cryoprotectants can be intimately mixed, or a whole fish fillet. Probably the most extensive applications of cryoprotectant molecules have been in the stabilization of surimi (e.g., cryoprotectants such as carbohydrates—particularly sugars and polyphosphates—only allowed in some countries) and to minimize the loss of protein functionality properties caused by the freezing and frozen storage processes on surimi. For whole-fillet applications, the most frequently used cryoprotectant to control the WHC is tripolyphosphate. It has been reported that the addition of polyphosphate will improve the texture and color of fish products (Gonçalves & Ribeiro 2008b, 2009; Gonçalves *et al.* 2008).

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31.6.3 Postfreezing treatments that protect frozen fish

Deterioration of seafood begins immediately upon harvest, and continues to various degrees depending on storage conditions. The best method of preserving seafood is freezing and storing at low temperatures. If properly frozen, seafood retains quality and flavor. A great problem encountered by producers of both fresh and frozen seafood is the dehydration of the product. Two protective methods are used, usually in combination: glazing and packaging. Good packaging prevents the circulation of air over the surface of the product and protects the moisture in the surface layers of the product (Gonçalves & Blaha 2010).

31.6.3.1 Glazing

Weight loss by dehydration during freezing and storage is directly proportional to the exposed surface area and can be reduced by two methods: covering the surface with packaging material, and surrounding the product with a thin layer of ice. The use of ice-glaze for small and irregularly shaped seafood products, like prawns and shrimp (individually quick frozen [IQF]), may be considered essential when stored without packaging or in pillow packs.

Glazing (or ice-glaze) means applying a coating of ice to the product that has already been frozen. Once frozen, the fish is sprayed with vaporized water, which immediately freezes into a thin layer on the surface of the fish. In this way, the entire surface of the fish is covered in an ice layer hindering air (oxygen) from getting in contact with the fish.

Generally, the glaze is simply water, but ingredients can be added (glycerin, sugar, phosphates, etc.). A glaze provides an excellent barrier to oxidation and freezer burn during frozen storage. Added ingredients include thickeners to ensure a good coating of glaze is applied, antioxidants to assist in preventing fat rancidity and color loss for whole fish, or sometimes just salt to maintain flavor. As soon as seafood is removed from a freezer, they should be glazed or wrapped (unless they have been packaged before freezing) and immediately transferred to a low-temperature store to rapidly refreeze and to preserve taste, smell, and texture as well as to minimize TD loss (Gonçalves & Blaha 2010).

According to Gonçalves and Gindri Junior (2009), a reasonable range of water uptake during the glazing process is between 15% and 20% to guarantee the final frozen shrimp quality. Nevertheless, abuse has been reported with coatings as thick as 25–45% (or up), but the most appropriate way to attain quality assurance is to introduce the standard procedures for ice-glazing, and complying to a regulated glazing content is important to the producers and consumers.

31.6.3.2 Importance of temperature monitoring

There are a number of papers that suggest that temperature fluctuations increase the rate at which fish quality is lost (Gonçalves & Blaha 2010). Indeed, Love (1969) suggested that due to a logarithmic relationship between quality loss and temperature, temperature fluctuation may greatly reduce quality and should therefore be avoided. Also, Scudder (1995) suggested that the degradation of TMAO to FA and DMA may have a maximum rate of around −18°C. Thus, it was recommended that the storage temperature on lean demersal fish should be between −24°C and −30°C. For oily fish, storage temperatures of −50°C to −60°C have been recommended in order to reduce the rate of oxidative changes (Magnussen 1992).

31.6.4 Future trends in frozen seafood

In the future, consumers are going to want more frozen seafood products and that that seafood should have a higher nutritional quality because of improvements in available varieties and in the handling of materials between harvest and processing. The textural quality and the retained nutritional content of frozen seafood after thawing will have improved by the new manufacturing processes, such as pressure shift freezing, that allow the production of smaller ice crystals during freezing. These products will be more stable because the ice crystals will remain small during distribution due to the incorporation of antifreeze proteins and other novel ice actives. Stability will also have improved by the formulation and the understanding of mobility and biochemistry in the unfrozen component. The distribution chain would be better controlled through the use of predictive modeling and through monitoring with time–temperature integrators (Kennedy 2000).

31.7 FINAL CONSIDERATIONS

It is possible to produce high-quality frozen fish if the physical and chemical changes described in this chapter are taken into account during handling immediately after catching, and in connection with the freezing and cold storage of the fish.

Temperature and temperature fluctuations are the most significant factors. It is important to cool the fish as quickly as possible immediately after it has been caught in order to minimize the biochemical and microbiological reactions from the very beginning. Fishing methods and temperature are likewise significant in relation to rigor mortis. In addition, it is essential that fish that are frozen, which will subsequently be thawed and processed, are frozen before rigor sets in, as this will result in the best eating quality and greatest yield.

The fish must be cleaned and bled before freezing, among other things because of the content of compounds in the blood that intensify the degradation processes and because of the very high enzyme activity in the guts.

Thus, a first-class frozen product can be achieved only when using entirely fresh fish and freezing them and storing them at low and stable temperatures. If subjected to poor handling in connection with freezing and cold storage, for example, in terms of a freezing process spanning a whole day and cold-storage temperatures that fluctuate over a longer time, the product will be ruined. Short-term storage of the raw material, gentle processing, quick freezing, short-term storage as a semiprocessed product, and short-term cold storage at temperatures lower than −30°C will result in the best product.

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